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## THEORY AND OPTIMIZATION OF SINTERING PROCESSES

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### I. INTRODUCTION

The goals of our research are the understanding of the time- and temperature-dependent evolution of clusters, cluster fusion, grain boundary transport and motion, and ultimately the development of a comprehensive, microscopic theory of sintering processes. In order to achieve these goals several scientific advances are necessary. A number of them require multidisciplinary efforts and benefit substantially from the diverse yet complimentary backgrounds of the principal investigators.

In order to be able to study theoretically the time evolution of cluster structures one has to develop fast and reliable methods for calculating total energies of fairly large clusters as well as forces on all the atoms. The requirements of speed, reliability and accuracy make this a rather difficult project, which will require considerable time and man-power. Its importance, however, cannot be overemphasized, since all microscopic modeling depends critically on this step. Our progress in developing these techniques is described in Section II.

Time-dependent microscopic simulations of cluster transformations and fusion are best carried out using molecular dynamics. For microscopic studies of sintering, the main issues are: (i) the dynamics of cluster transformations as a function of temperature; (ii) the identification of the mobile pool of atoms; and (iii) the mechanisms of atomic motion. For now, we have mainly focused on cluster melting and the results of our studies to date are

described in Section III.

Larger clusters and "real" sinters consist of too many atoms to make atomistic calculations practical. Fortunately, most of the microscopic phenomena important to sintering can be accounted for in a continuum theory with parameters derived from microscopic calculations. Furthermore, a number of very useful and general conclusions about the sintering process can be drawn by considering the shrinkage of close-packed clusters under the influence of surface tension forces. We have already made considerable progress in this area in studies of first stage sintering. Our current work is discussed in Section IV.

## **II. CLUSTER ENERGETICS AND INTERATOMIC POTENTIALS**

The microscopic modeling of the time-evolution of clusters requires either the development of highly reliable classical potentials or the use of very expensive, although highly accurate, quantum-mechanical time-dependent techniques, such as the Car-Parinello method. Due to the size of the clusters needed to study sintering and cluster melting, only the first option is practical. The starting point for this part are the existing classical potentials, but they have to be adapted for small and medium size clusters and their reliability needs to be checked not only against the available experimental data but also against metastable and unstable atomic configurations. We have selected to study Cu and Al first, since the existing potentials already reproduce bulk and surface properties fairly well. However, these cases should be considered as paradigmatic. The same techniques will be used to generate potentials for other elements as soon as enough experience has been accumulated.

For copper, we have carried out local density calculations using the discrete variational method (DVM) for closed packed clusters containing 6, 9, and 15 atoms. Not surprisingly, we found that the embedded atom potentials do not describe the clusters with the same accuracy as bulk properties. We are at present working on improving these potentials by both refitting the potential parameters and by adding extra terms to the potential. We are also exploring the effective medium approach for clusters, since this method allows for systematic improvements in the quality of the potentials. However, some of these improvements may lead to complicated potentials which are too computer time intensive for use in molecular dynamics simulations. Therefore, the resulting potentials may have to be reparametrized.

For Al clusters and other non-transition metal systems, we are setting up Car-Parinello calculations, which combine local density theory with molecular dynamics. We have already obtained the codes from the Car-Parinello group and are modifying them to study clusters.

The quantum-mechanical calculations will be used to both generate the database for fitting the interatomic potentials and to check their accuracy by comparing the results of quantum-mechanical simulations to those carried out using the interatomic potentials for exactly the same system. In the future, we will also attempt to adapt the Car-Parinello method for studies of transition metals.

In order to interface with our continuum modeling effort, we must develop techniques for extracting macroscopic information, such as diffusion coefficients, from the simulations. Our initial tests on a 33-atom Cu cluster showed the free energy of cluster remains sufficiently stable during the course of a short, low temperature simulation that the entropy of the system can be obtained from the relation  $S = -\partial F / \partial T$ . These results were obtained using the embedded atom method, but the short time of the simulation suggests that it will be possible to calculate entropic contributions via ab-initio molecular dynamics.

### III. STUDIES OF CLUSTER MELTING

The brief period covered by this report has already been productive. Simulations by classical molecular dynamics have been carried out at The University of Chicago in order to begin the study of surface melting and of the mobility of atoms on the surface of clusters. Prior work at Chicago and elsewhere had shown that very small clusters, 33 particles or fewer, show no such thing as surface melting. Such small clusters may be solid-like, or like homogeneous liquids, or in some instances soft but restricted to oscillations around a few specific geometric configurations. Only a very few, scattered studies had been made of even slightly larger clusters, most notably the 55-atom argon cluster, because of its "closed-shell" icosahedral structure.

Results for Ar<sub>55</sub> had been controversial. One study had reported no indication of surface melting, and the one other addressing the question had arrived at exactly the opposite conclusion. We have now investigated the surface melting of this cluster and several others slightly smaller and slightly larger. There is now no question; Ar<sub>55</sub> does exhibit surface melting whether it is subject to free boundary conditions or is confined to a large, fixed volume. Furthermore, some clusters slightly smaller than the closed-shell icosahedron, certainly Ar<sub>52</sub> and probably Ar<sub>46</sub>, show surface melting but Ar<sub>45</sub>, Ar<sub>43</sub> and Ar<sub>39</sub> do not. These results are firm but just preliminary in the sense of a systematic study of surface melting. Obviously, the objectives of this study will not be met by studying clusters of argon; we have begun parallel simulations based on a model for copper, but the potential surface we have used thus far is still too crude and inaccurate to be used for any serious judgments about real copper clusters. Programming is now underway also to treat clusters of salt-like molecules, notably alkali halides.

More interesting and more important than the finding regarding the sizes of clusters exhibiting surface melting is the new insight regarding what surface melting is. The simulations of argon clusters have shown now that the *two* outer layers of a cluster become mobile when the surface of the cluster melts. It is not just the outermost layer, but also the next layer, not completely covered in the solid form of the cluster, which become mobile and show diffusion, soft modes and the disorder and permutations characteristic of liquid phases.

Some very recent results now show that the 55-atom cluster of copper, represented by a rather approximate embedded-atom type potential, exhibits surface melting. This means that it will be feasible to begin modeling the sintering process with clusters as small as 55 atoms. Smaller copper clusters, at least of some sizes, do not exhibit surface melting. Furthermore, like argon clusters, the outer two layers, rather than just the outermost layer, are involved in surface melting.

This work is now just at the stage of developing enough examples for which surface melting is unambiguous; from these examples we will go on to compute the mobilities of atoms in the liquid (or simply mobile) surface phase. Those mobilities are one of the two key sets of microscopic parameters needed to complete our theoretical model of sintering. The other set constitutes the corresponding mobilities along grain boundaries, since sintering depends on the transport of material primarily by these two routes, and the specific mechanism depends on their relative importance as fixed by the corresponding mobilities.

#### **IV. MACROSCOPIC MODELS OF SINTERING**

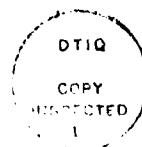
We have been pursuing solutions to the shape of a sintered material based on a model which uses separability of time scales between the formation of a mobile pool of material and its redistribution over the surface. The formation of the mobile pool is assumed to be slow and the dynamical model for this will require several parameters from the groups in Chicago and at NCSU. The redistribution of the mobile phase occurs in a fashion which minimizes the surface area of the sinter and thus results in shapes which can be explored analytically and numerically.

The problem in two dimensions is analytically tractable. We have gained considerable insight from the solutions obtained for several model porous media. Briefly, each pore may be characterized by a curve giving the mean curvature  $K$  of its wetted surface as a function of the volume of material  $V$  added to the pore. The importance of the mean curvature derives from the fact that the chemical potential difference between different points on the surface of the pore is

mean curvature derives from the fact that the chemical potential difference between different points on the surface of the pore is proportional to the mean curvature. Under mild hypotheses, the curves  $K(V)$  display simple universal features which can be exploited in models of the pore-to-pore redistribution of mobile material. Notably, they have a vertical asymptote at  $V=0$  where the curvature is negative infinity, increase monotonically to a maximum (negative) value at  $K$  corresponding to the largest sphere which can be inscribed in the pore, and then decrease monotonically to minus infinity at a second vertical asymptote at  $V$  equal to the volume of the pore. The latter decrease follows a universal curve for all pores. This allows a distribution of pores to be modeled conveniently and realistically using only a few parameters. These models predict shapes and dynamics and have important implications for second and third stage sintering when the pore-pore interactions become dominant.

For first stage sinters the three dimensional model has been reduced to solving an ordinary differential equation. We have examined different shooting methods for solving the equations for the necks formed between particles based on Adams and Runge-Kutta integration schemes. While using these schemes we have been able to work out solutions for lattices of spheres and for two spheres with different radii, fitting the solutions remains a difficult problem. A manuscript is under preparation detailing the implications of the two sphere solutions to the problem of grain boundary disappearance. Explorations of the possibility of directly fitting the elliptic function solutions have progressed to a careful study of the solution curves directly from the differential equation and promise superior methods for fitting the solutions to boundary data.

Simulations of sintering shapes using lattice gas models has been successful using two methods: Monte Carlo and mean field. The methods are simple and powerful. The graphical outputs from these models agree with each other and with physical intuition. Analytical studies of the interaction of spherical pores in two and three dimensions are being undertaken to complement the simulations. In addition, we are investigating a modification of the Lifschitz-Slyozow model to apply to three dimensional pores connected via two dimensional grain boundaries.



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